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(54) **Tobacco smoke filter element with alkali ferrate supported on granular material.**

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Tobacco smoke filter element with alkali ferrate supported on granular material

This invention relates to a tobacco smoke filter element comprising a granular support material having thereon an alkali metal and/or alkaline earth metal ferrate, one or more additives being optionally admixed with the treated support material. The filter element may be used so as to selectively remove at least partly some undesirable constituent from tobacco smoke, for example a gas such as hydrogen cyanide, though the content of one or more other undesirable constituents may likewise be reduced.

The filter element of this invention is used as a filter for cigarettes, cigars or other smoking articles, which filter is effective in the removal of one or more undesirable smoke phase components, e.g. hydrogen cyanide and ammonia.

Methods for selective removal of hydrogen cyanide from cigarette smoke by means of special filter compositions have been proposed. For example, U.S. Patent 3,664,352 discloses alkaline additives such as alkali metal carbonates which may be applied to conventional filter materials to remove any hydrogen cyanide contained in tobacco smoke. Activated carbonaceous material with a surface treatment of copper oxide has also been proposed for hydrogen cyanide removal. U.S. Patents 3,251,365, 3,460,543, and 3,355,317 disclose various metal oxides, namely oxides of cobalt, copper, zinc or iron, on a carrier for removal of hydrogen cyanide. U.S. Patent 3,550,600 discloses zinc acetate in admixture with an organic or inorganic base on a smoke filter paper or cellulose acetate filter support which is described as being effective in the removal of various gaseous components, including hydrogen cyanide, from tobacco smoke.

U.S. Patent 3,828,800 discloses certain anion exchange resins which have an affinity for volatile aldehydes as well as the capability to filter other components such as hydrogen cyanide. U.S. Reissue 28,858 discloses buffered polyalkyleneimines which exhibit an affinity for smoke acids.

U.S. Patents 3,946,101, 3,875,949, and 3,842,070 disclose a complex fluid filter comprising cellulose which has been oxidized by an inorganic metal nitrate. The filter is described as being useful in removing gaseous and particulate components of smoke.

U.S. Patent 3,618,619 discloses filters fabricated from cellulose acetate which has been impregnated with metal oxides of zinc, iron, copper, etc. and are effective in removing hydrogen cyanide.

U.S. Patent 3,417,758 discloses filters containing a water-soluble, weak basic inorganic salt, i.e., sodium or potassium phosphite, which are described as effective in neutralizing hydrogen cyanide in tobacco smoke.

U.S. Patent 4,022,223 discloses salts of copper and nickel complexed with selected aliphatic or aromatic amines which effectively remove hydrogen cyanide from tobacco smoke.

Although many of the aforementioned additives are effective in reducing hydrogen cyanide in smoke, certain disadvantages remain from a smoker's viewpoint. In some instances, volatile flavorants are removed, thus altering the desirable subjective characteristics. In addition, some of the additives may give an off-taste which renders them undesirable for smoking articles. Other methods or additives discussed hereinabove are not suitable due to the unstable nature of the compounds used or to the expense in preparing them.

It is, therefore, a purpose of the present invention to overcome or minimize the disadvantages noted above and to provide a filter element capable of selectively removing undesirable constituents, e.g. hydrogen cyanide, from tobacco smoke.

In one of its aspects, the present invention provides a tobacco smoke filter element comprising an inert gas-permeable granular support material having thereon an alkali metal or alkaline earth metal ferrate, said ferrate being present in an amount from about 15 to about 50% by weight of said material said ferrate being an iron compound having an oxidation state of+4, +5 or +6.

The advantages of the present invention will become apparent from the detailed description of the invention.

The additives for treating the gas-permeable granular support material are iron compounds in oxidation state of +4, +5 and +6 associated with oxygen in an anion radical. Such compounds are known and are generally referred to as ferrate (IV), ferrate (V) and ferrate (VI). The preferred compounds of the invention are the alkali and alkaline earth salts of ferrate (VI). The most preferred individual compound is potassium ferrate (K_2FeO_4), though sodium ferrate (Na_2FeO_4) is also highly suitable.

The ferrate compounds used in the present invention have been investigated previously for use in water purification systems and specifically for the oxidation of ammonia in water. (See *Oxidation of Ammonia in Water by Ferrates (VI) and (IV),* Svanks, Karlis. Project Completion Report No. 444, Water Resources Center, Ohio State University, Columbus, Ohio.) In addition, alkaline ferrate (VI) in combination with a ferrite solution has been used for removing hydrogen sulfide from a low-pressure gas by adsorption. The hydrogen sulfide present in the gas is oxidized to sulfur and may be recovered. (See Japan Kokai 74:37,894.) The

use of ferrates for the removal of gas phase components of tobacco smoke, and specifically, hydrogen cyanide has not been proposed heretofore.

Granular substances which may be employed in forming a gas-permeable bed must, of course, be substantially inert to the alkali metal and/or alkaline earth metal ferrates; they may consist of (a) inorganic substances, e.g. silica gel, activated alumina, magnesia, calcium sulfate, diatomaceous earth, perlite, and still other inorganic substances; (b) organic substances such as polyethylene (e.g. microporous polyethylene powder), polystyrene, and still other organic substances; and (c) molecular sieve materials such as zeolites. The granular substance is preferably porous to the extent of having a pore volume between about 0.1 and 2.5 cc per gram.

When the granules are utilized as a gas-permeable bed in a cigarette filter, they should be chemically inert, porous and have a size ranging from about 10—100 mesh (U.S. Sieve Series, ASTME—11—61) and preferably a range of 20—80. In expressing granule size by mesh numbers, it is to be understood that each range signifies that granules will pass through the coarser sieve designated (the smaller sieve number) will be retained on the finer sieve designated (the larger sieve number). Granules having a size finer than about 100 mesh generally impart too high an impedance to gas flow. Granules larger than about 8 mesh provide reduced efficiency of removal of hydrogen cyanide.

The potassium ferrate (VI) compounds are readily prepared by the method of Thompson et al. (*Journal of the American Chemical Society, 73,* 1951, page 1379) utilizing the reaction of sodium hypochlorite with ferric nitrate and subsequent conversion to the potassium salt. The purified, dried potassium ferrate is obtained in the form of very fine crystalline needles having an average length less than about one millimeter. The ferrates (VI) may also be prepared from ferrates (IV) by methods disclosed in U.S. Patent 2,835,553. Sodium ferrate (Na_2FeO_4) may be prepared by methods disclosed in German Patent 1,013,272 (8 August 1957).

The ferrate-containing granules may be dry-blended with other granular material useful in cigarette filters in a weight ratio of about one part ferrate-containing granules to three parts of other granular materials and preferably at a ratio of about one to one. It has been found that the presence of strongly alkaline compounds in admixture with the ferrates improves storage stability. In the absence of the alkaline compounds, the ferrates will decompose on standing at room temperature. Alkaline compounds suitable as stabilizers for the ferrates include potassium hydroxide and sodium hydroxide.

In a preferred embodiment of the invention, the ferrate crystals are dissolved in a concentrated aqueous hydroxide solution which is then used to impregnate a granular support, preferably a zeolite molecular sieve. The impregnated granules are then treated with a stream of carbon dioxide gas to convert the alkaline hydroxide to its corresponding carbonate salt. The impregnated material is then dried at temperatures below about 100°C, and preferably at temperatures from about 0°C. to about 50°C. The drying step may be carried out with the aid of a vacuum or a stream of dry inert gas such as nitrogen. The extent of drying is such that the granules will retain from about 2% to about 10% moisture. Overdrying of the ferrate impregnated material may result in loss of storage stability.

The active ferrate filter materials whether dry-blended or impregnated on various supports may be used alone in a filter element or may be blended with other known granular materials having gas phase activity such as activated carbon and permanganate-impregnated alumina. For this purpose, the activated carbon is a variety generally employed for gas adsorption, having a surface area of at least about 800 m^2/gm, and ranging as high as about 1600 m^2-gm. The carbon granules are preferably employed in an amount of from about 30 to about 50% by weight of the total mixture. When permanganate is used, it is preferable to employ essentially silica-free activated alumina granules impregnated with an aqueous permanganate solution and a basic sodium compound according to methods disclosed in U.S. Patent 3,957,059 to Rainer et al. Basic sodium compounds which may be used include sodium hydroxide, sodium carbonates, sodium phosphates, and sodium borates. The permanganate-alumina composition when blended with the ferrate filter material enhances the overall efficiency of the combined filter in that it is especially effective in reducing the amount of nitrogen oxides which may be present in tobacco smoke.

It is thus within the scope of the invention to admix the filter material with from about 15 to about 50% by weight of granules of essentially silica-free alumina impregnated with a solution of sodium permanganate in combination with a basic sodium compound.

The filter material whether employed per se or in admixture with other materials can be utilized as a bed in a space between plugs of a standard cellulose acetate filter rod. The filter assembly is then abutted against a cylinder of tobacco, and a paper wrapper may be employed to fasten the filter to the tobacco rod. Alternatively, the filter material may be separate from the smokable tobacco product, such as a filter unit adaptable for use with a cigarette or cigar holder. In a similar fashion, a filtering device employing the material of this invention can be appropriately packed into the stem of a tobacco pipe. In all such filter configurations,

the granule-containing filter will have a resistance to draw (RTD) of less than about 127 mm of water when measured at an air flow velocity of 1050 cc/minute. Acceptable RTD and hydrogen cyanide removal can be achieved by using from about 50 to 400 mg of the filter material of the invention in the specified mesh size.

For the purposes of this invention, hydrogen cyanide determinations on cigarette smoke were carried out by infrared analysis which provides a value representation of the hydrogen cyanide present in the gas stream. By this method, it has been found that the filter material of this invention is capable of reducing the hydrogen cyanide content of tobacco smoke by about 25 to about 70%.

It will be understood that still other materials generally known in the cigarette filter art may be utilized to either selectively remove other components of the smoke, or flavor compounds may be used in combination with the filter material.

The following examples are illustrative.

Example 1

Forty parts of potassium ferrate crystals (K_2FeO_4) prepared according to the method of Thompson et al., were dry blended with 60 parts of a microporous polyethylene powder having a 40/80 mesh size. Sixty milligrams of this mixture were placed in a 10 mm long cigarette filter compartment bounded by two 6 mm long plugs of 8 mm diameter cellulose acetate filter rod comprised of 8 denier filaments in a bundle having a total denier of 40,000. The entire filter assembly, having an 8 mm cylindrical diameter, was wrapped with a stiff nonporous paper.

The filter assembly was attached to an end of a Kentucky IRI Reference cigarette described in a research bulletin entitled *The Reference Cigarette* published by the University of Kentucky, 29 August 1964. The overall RTD of the cigarette and filter combination was 127 mm of water when measured at an air flow velocity of 1050 cc/minute. Two cigarettes were simultaneously smoked on an electric smoking machine which drew air through the lit cigarette in puffs of 2 seconds duration, 35 cc of air/puff, and permitting 58 seconds of static burn between puffs. The smoke from 8 puffs was passed through a Cambridge filter pad to remove total particulate matter. The resultant gas phase of the smoke was combined through a common manifold and collected in a previously evacuated one meter infrared gas cell. The gas in the cell was then subjected to infrared spectroanalysis, using a Perkin-Elmer 221 infrared spectrophotometer with ordinate scale expansion. Three replicate samples were taken. The identical procedure was used with control cigarettes which were identical to the cigarettes c mbined with the filter material except that the 10 mm compartment was filled with untreated microporous polyethylene. Comparison of the absorption band height from the cigarette.c mbined with the filt r material and the control cigarettes indicated that a 28% reduction in HCN was achieved by the filter material of the invention. No other measured components of the smoke were affected. The taste of the cigarette was essentially unchanged from that of a control cigarette. By way of comparison, the untreated microporous polyethylene filter provided cigarette smoke showing no reduction in HCN content.

Example 2

Potassium ferrate, prepared by the aforesaid procedure, is dissolved to saturation in an aqueous 10 molar solution of potassium hydroxide. The resultant solution was utilized to impregnate to saturation 20/40 mesh granules of a zeolite molecular sieve material (type SK—40, sold by the Ventron Company of Beverly, MA). The impregnated granules were treated with a stream of CO_2 gas to convert the potassium hydroxide to potassium carbonate, and the resultant product was dried. Two hundred fifty mg of this material was loaded into filters of the same construction utilized in Example 1, and the filters were mounted onto tobacco rods. The overall cigarette and filter RTD was 127 mm of water. The potassium ferrate present in each filter was within the range of about 15 to about 50% by weight.

Testing of the smoke delivered through the filters was carried out in the same manner described in Example 1. It was found that a 66% reduction in HCN content of the gas phase of the smoke was produced. Little measurable effect was produced on other components, as judged by IR analysis of gas phase. There was no evidence (such as discoloration) to show potassium ferrate emerging into the smoke stream, and the cigarette smoke had acceptable flavor. A control filter, prepared from the granular molecular sieve material without addition of the potassium ferrate solution, produced a 12% reduction in HCN content of the smoke.

Example 3

Potassium ferrate-impregnated molecular sieve granules, as prepared by the method of Example 2, were blended with an equal weight of 20/40 mesh size granules of alumina impregnated with sodium permanganate sodium hydroxide in accordance with U.S. Patent 3,957,059 to Rainer et al.

Two hundred fifty mg of the blended granular mixture was loaded into filters of the same construction utilized in Example 1, and the filter assembly was attached to an end of Kentucky IRI Reference cigarettes. Th overall RTD of the cigarette and filter combination was 127 mm of water when measured at an air flow velocity of 1050 cc/minute. The potassium ferrate present in each filter was within the range of

ab ut 15 to about 50% by weight. The cigarettes were smoked and the resultant smoke was analyzed by the methods of Example 1.

It was found that the smoke produced by the cigarettes of this example delivered 85% less HCN and 65% less oxides of nitrogen than the same cigarettes having only a conventional cellulose acetate filter plug.

When the filter assembly was made to contain solely the alumina granules impregnated with sodium permanganate/sodium hydroxide, the reduction in amount of HCN in the delivered smoke was only 60%, and the reduction in delivered oxides of nitrogen was only 48%.

Claims

1. A tobacco smoke filter element comprising an inert gas-permeable granular support material having thereon an alkali metal or alkaline earth metal ferrate, said ferrate being present in an amount from about 15 to about 50% by weight of said material, said ferrate being an iron compound having an oxidation state of +4, +5 or +6.

2. A tobacco smoke filter element according to Claim 1, wherein said ferrate is an alkali or alkaline earth metal ferrate VI.

3. A tobacco smoke filter element according to Claim 1 or 2, wherein said granular support has been impregnated with potassium ferrate VI in admixture with potassium hydroxide, said hydroxide having been subsequently converted to carbonate.

4. A tobacco smoke filter element according to Claim 1, 2 or 3, wherein said granular support is a zeolite molecular sieve or microporous polyethylene powder.

5. A tobacco smoke filter element according to any one of the preceding claims admixed with from about 30 to about 50% by weight of activated carbon having a surface area of from about 800 m^2/gm to about 1600 m^2/gm.

6. A tobacco smoke filter element according to any one of the preceding claims admixed with from about 15 to about 50% by weight of granules of essentially silica-free alumina impregnated with a solution of sodium permanganate in combination with a basic sodium compound.

7. A tobacco smoke filter element according to any one of Claims 1 to 4 stabilized by an alkaline compound and having a moisture content of about 2% to about 10%.

Revendications

1. Elément de filtration pour fumée de tabac comprenant matériel de support granulé perméable à gaz ayant un ferrate d'un métal alcalin ou terre alcaline, la quantitée de ferrate présent étant approximativ ment 15 à appr ximativement 50% en p ids, le ferrat étant un composé de fer ayant un état d'oxydati n de +4, +5 u +6.

2. Elément de filtration sel n revendication 1, caractérisé par le fait qu le f rrate est un ferrate (VI) d'un métal alcalin ou terre alcaline.

3. Elément de filtration selon revendication 1 ou 2, caractérisé par le fait que le support granulé a été imprégné avec du ferrate potassié (VI) mélangé avec de l'hydroxyde potassié, ce dernier ayant été converti préalablement au potasse carbonaté.

4. Elément de filtration selon revendication 1, 2 ou 3, caractérisé par le fait que le support granulé est un tamis moléculair zéolithique ou de la poudre de polyéthylène microporeuse.

5. Elément de filtration selon l'une des revendications 1 à 4, caractérisé par le fait qu'il est mélangé avec approximativement 30 à approximativement 50% en poids de carbone activé ayant une surface mesurant approximativement 800 m^2/g à approximativement 1600 m^2/g.

6. Elément de filtration selon l'une des revendications 1 à 4, caractérisé par le fait qu'il est mélangé avec approximativement 30 à approximativement 50% en poids de matériel granulé d'alumine essentiellement sans silice imprégné avec une solution de permanganate de natrium en combinaison avec un composé de natrium basique.

7. Elément de filtration selon l'une des revendications 1 à 4, caractérisé par le fait qu'il est stabilisé par un composé alcalin et contenant approximativement 2% à approximativement 10% d'humidité.

Patentansprüche

1. Tabakrauch Filterelement aus einem Inerten gasdurchlässigen granulierten Unterlagsmaterial mit einem Alkalimetall- oder alkalischen Erdmetallferrat, welches Ferrat in einer Menge von ungefähr 15 bis ungefähr 50 Gewichtsprozenten gegenwärtig ist und eine Oxydationsstufe von +4, +5 oder +6 aufweist.

2. Tabakrauch Filterelement nach Anspruch 1, in welchem das Ferrat ein Alkalimetallferrat (VI) oder alkalisches Erdmetallferrat (VI) ist.

3. Tabakrauch Filterelement nach Anspruch 1 oder 2, in welchem das granulierte Filtermaterial mit Kaliumferrat (VI) vermischt mit Kaliumhydroxyd imprägniert worden ist, welches Hydroxyd später zum Carbonat umgewandelt worden ist.

4. Tabakrauch Filterelement nach Anspruch 1, 2 oder 3, in welchem das granulierte Unterlagsmaterial ein zeolithisches Molekülsieb oder Polyätylenpulver ist.

5. Tabakrauch Filterelement nach einem der vorangehenden Ansprüchen vermischt mit ungefähr 30 bis ungefähr 50 Gewichtsprozenten Aktivkohle mit einem Oberflächenareal von ungefähr 800 m^2/g bis ungefähr 1600 m^2/g.

6. Tabakrauch Filterelement nach einem der vorangehenden Ansprüchen vermischt mit

ungefähr 30 bis ungefähr 50 Gewichtsprozenten granuliert n Material aus im Wesentlichen Silicium xyd freien Aluminoxyd, welches mit einer Lösung von Natriumpermanganat in Kombination mit einer basischen Natriumverbindung imprägniert ist.

7. Tabaakrauch Filterelement nach einem der Ansprüche 1 bis 4 stabilisiert mit einer alkalischen Verbindung welche einen Feuchtigkeitsgehalt von ungefähr 2% bis ungefähr 10% aufweist.